Investigating preferential adsorption of N_2 from the air in Zeolite 13X using total neutron scattering

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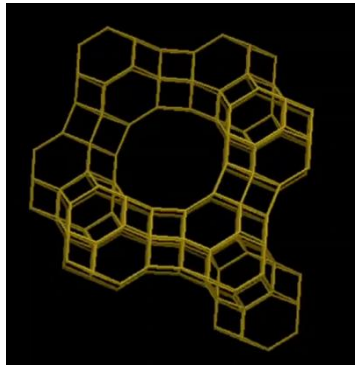
Medical oxygen concentrators

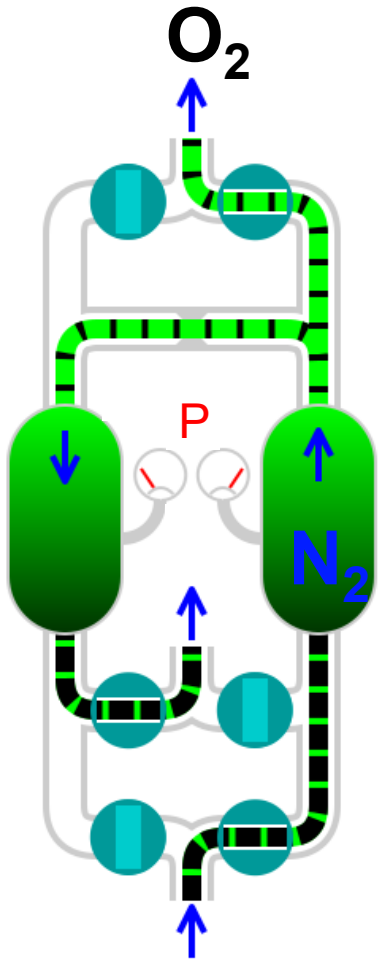
- High purity oxygen (up to 92 vol%) produced in a continuous and reliable way
- 2 zeolitic beds working in adsorption – desorption cycles
- Utilisation of pressure swing adsorption

Medical Oxygen Concentrator

Zeolite 13X



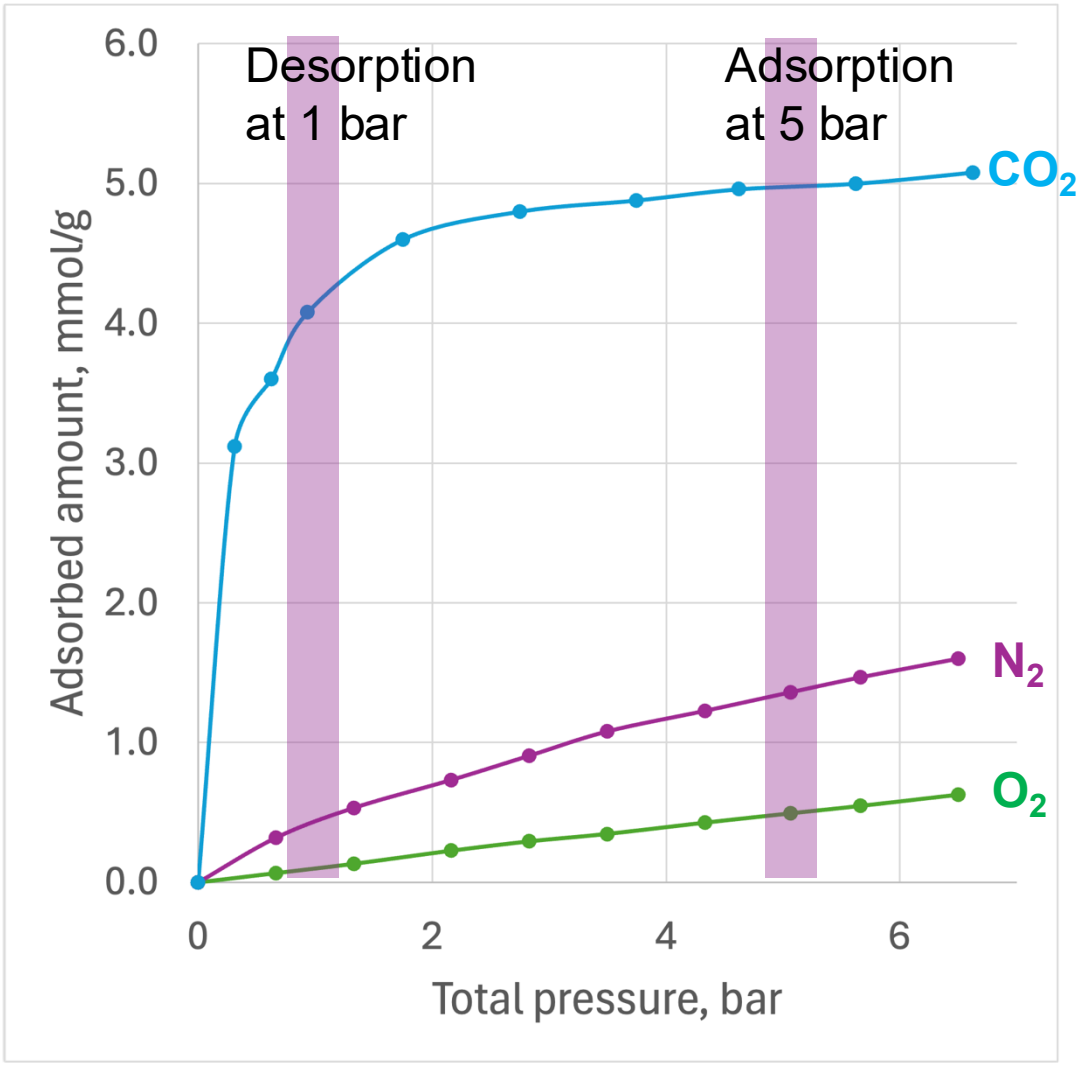
Surface area: 769 m^2/g
Pores openings: 7.4 Å

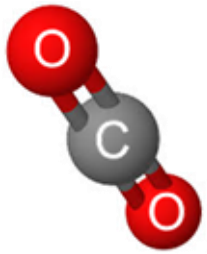


Compressed Air

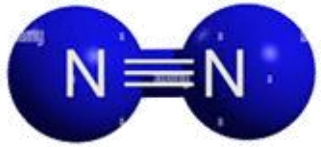
Preferential adsorption of N_2 at 293 K

Zeolite 13X

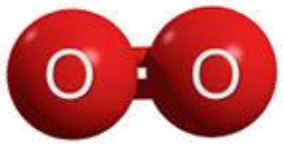




*Quadrupole moment:**
-4.3×10^{-26}



*Quadrupole moment:**
-1.4×10^{-26}



*Quadrupole moment:**
-0.4×10^{-26}

** In esu/cm^2*

N_2 & O_2 data: Mofarahi *et al*.,Petrol. & Coal 2013, 55, 216

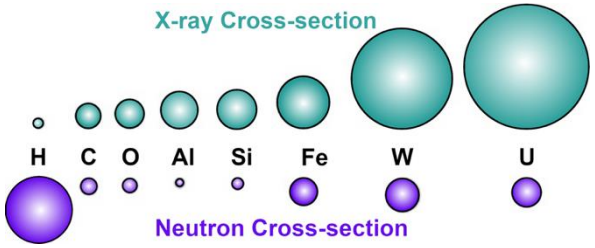
CO_2 data: Golubyatnikov *et al*., Sep Sci Technol, doi.org/10.1080/01496395.2022.208410, 2022

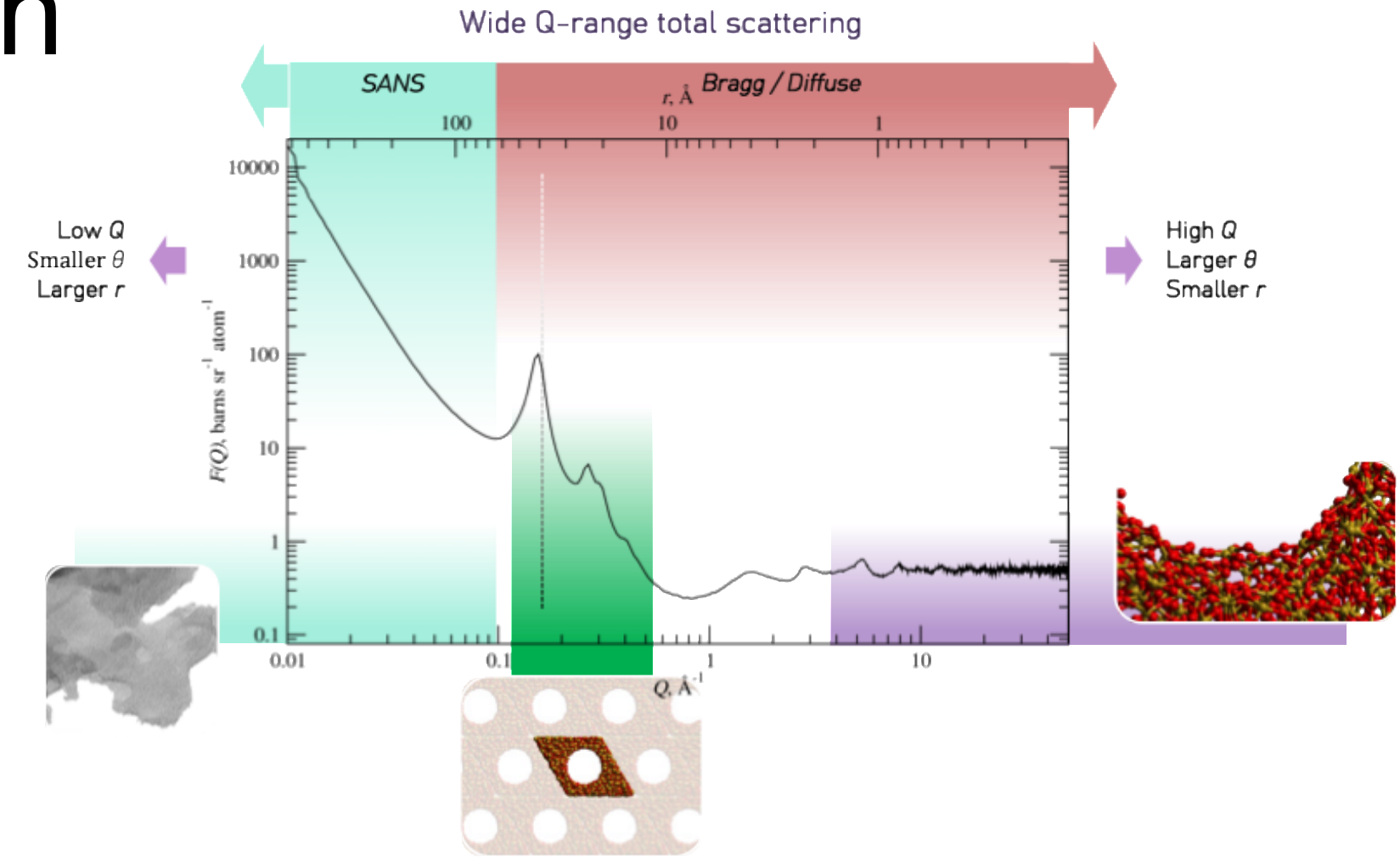
Total neutron scattering

Near and InterMediate Range Order Diffractometer (NIMROD) with *Q*-range of 0.01 to 50 Å^{-1}

Science and Technology Facilities Council

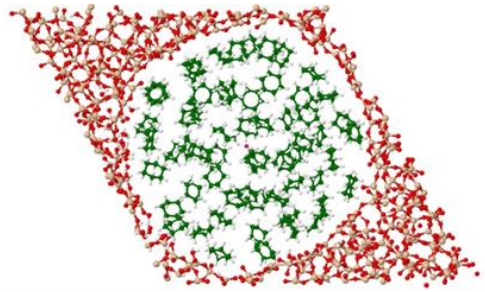
ISIS Neutron and Muon Source



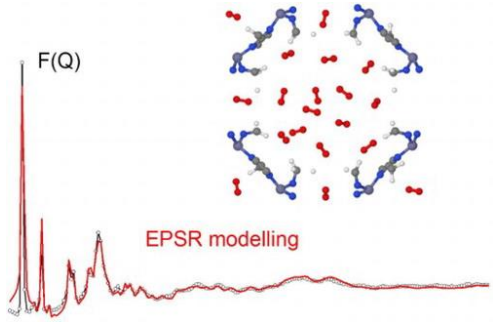


- A single total structure factor collected at NIMROD contains information across multiple length scales, *i.e. from mesoscopic properties to interatomic interactions.*

Adsorption studied by TNS



Benzene in MCM-41[6]

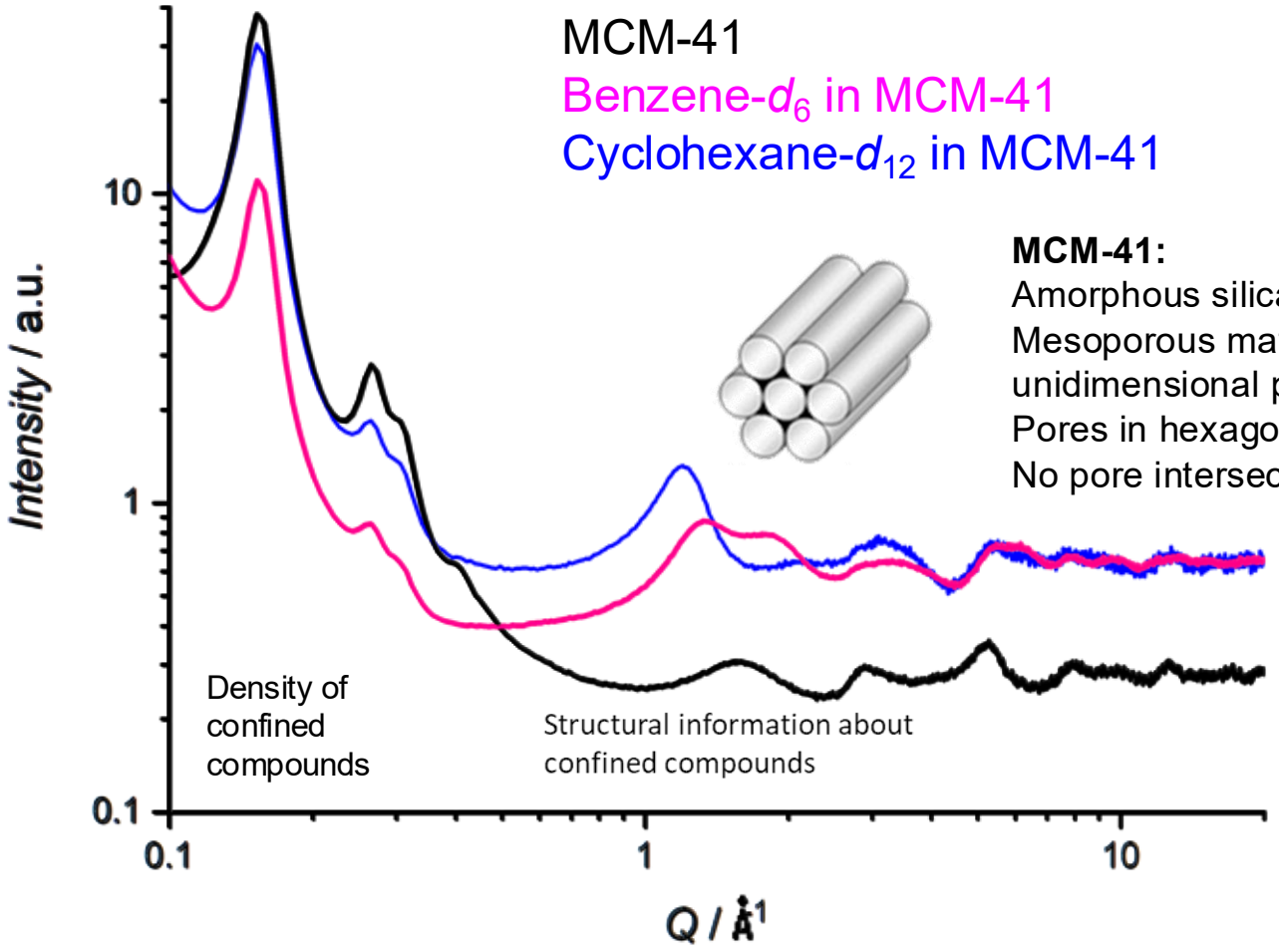


O_2 in ZIF-8[3]

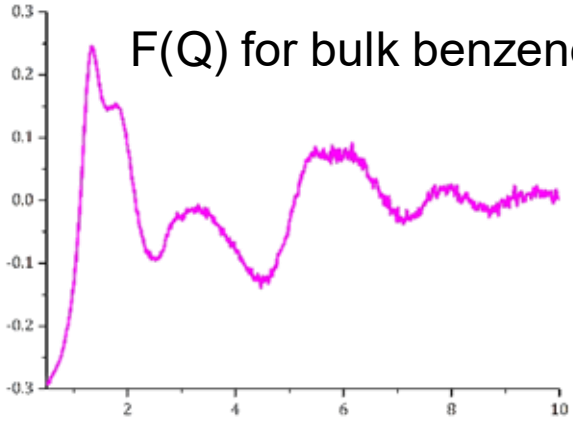
Study	Gas	Solid	Temperature
1	CO_2	CMK-3	195-235 K
2	CD_4, N_2, D_2, O_2	MCM-41	25-146 K
3	O_2	ZIF-8	85 K
4	N_2	MCM-41	87 K
5	CO_2	SBA-15	195-214 K
6	Benzene	MCM-41	**293 K**
This work	N_2, O_2, Air, CO_2	Zeolite 13X	**293 K**

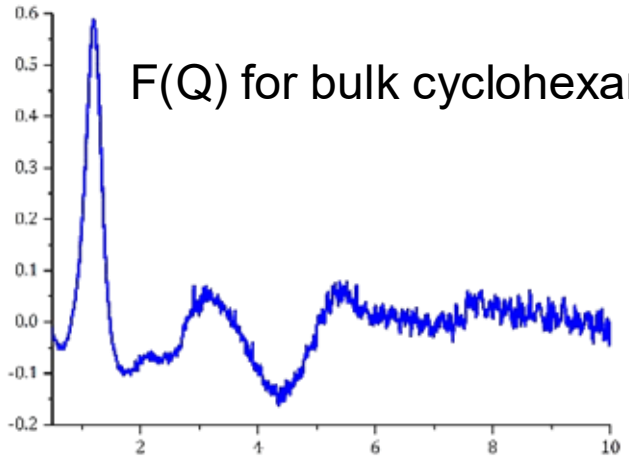
1. Total neutron scattering study of supercooled CO_2 confined in an ordered mesoporous carbon – K. Stefanopoulos *et al*., Carbon 2020, 167
2. Adsorption of simple gases into the porous glass MCM-41 – A. Soper and D. Bowron, J. Chem. Phys. 2021, 154
3. Oxygen condensation in ZIF-8 upon ‘gate opening’ structural transition – R. Boada *et al*., Molecular Physics 2019, 117
4. Density profile of nitrogen in cylindrical pores of MCM-41 – A. Soper and D. Bowron, Chemical Physics Letters 2017, 154
5. Anomalous Depletion of Pore-Confined Carbon Dioxide upon Cooling below the Bulk Triple Point: An in Situ Neutron Diffraction Study – K. Stefanopoulos *et al*., Physical Review Letters 2016, 116
6. **Confinement Effects on the Benzene Orientational Structure – M. Falkowska *et al*., Angewandte Chemie 2018, 57**
7. **Molecular Insights into Preferential N_2 Adsorption on Zeolite 13X via Total Neutron Scattering, Falkowska et al., Adsorption 2025, 31**

Liquids in pores



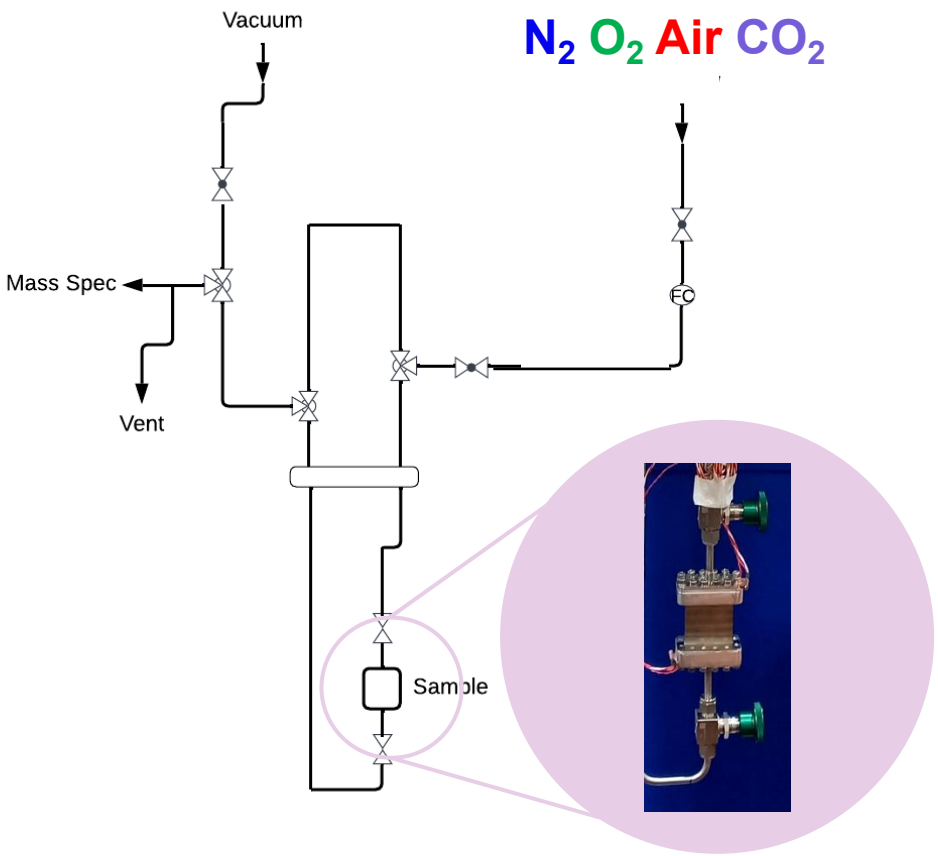
MCM-41:
Amorphous silica
Mesoporous material with uniform unidimensional pores
Pores in hexagonal arrangements
No pore intersections





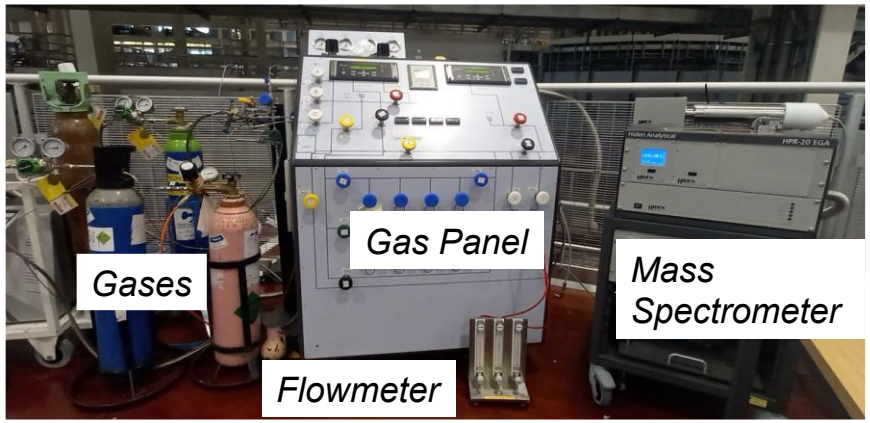
Would this work for gases at RT?

Experimental protocol

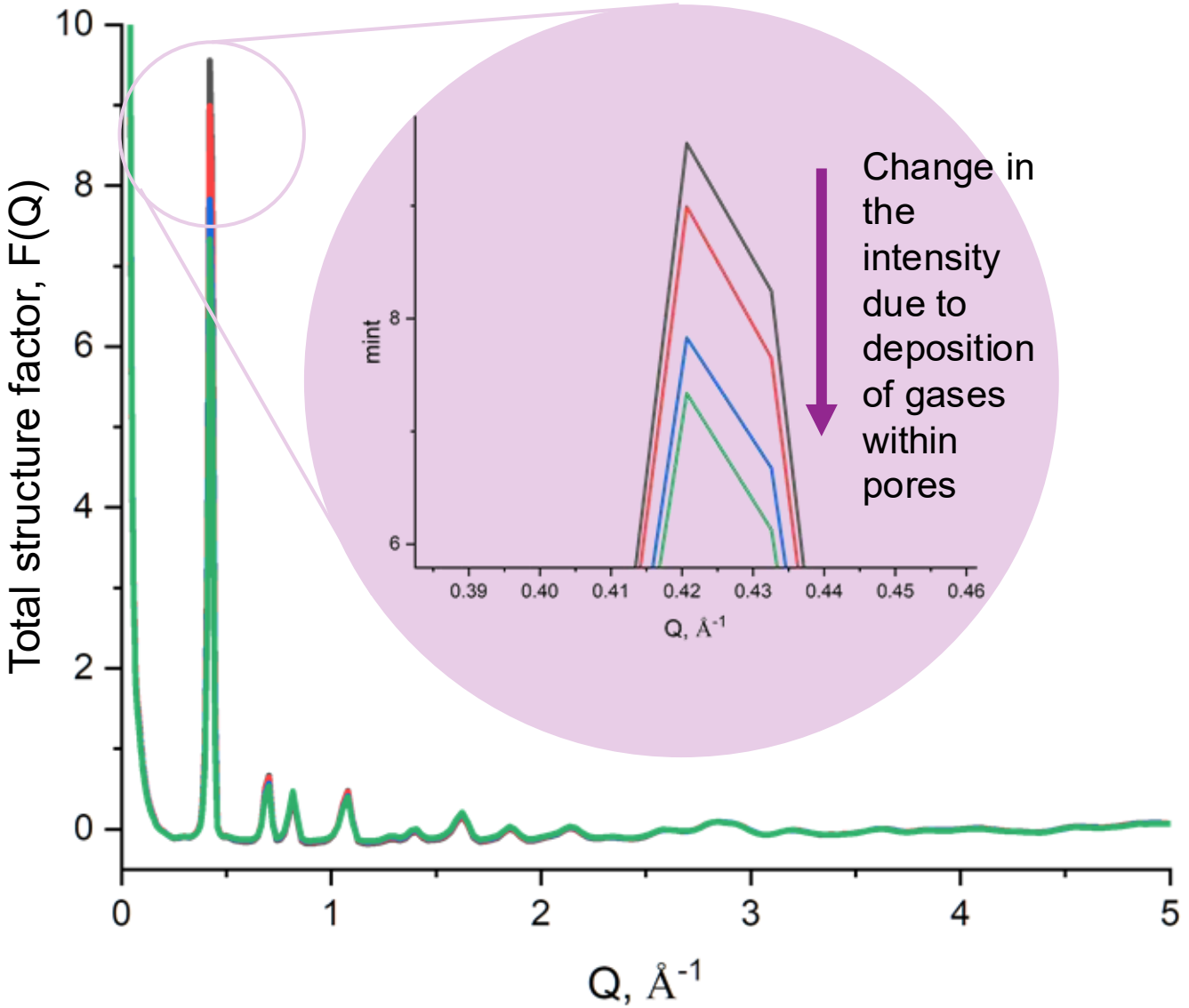


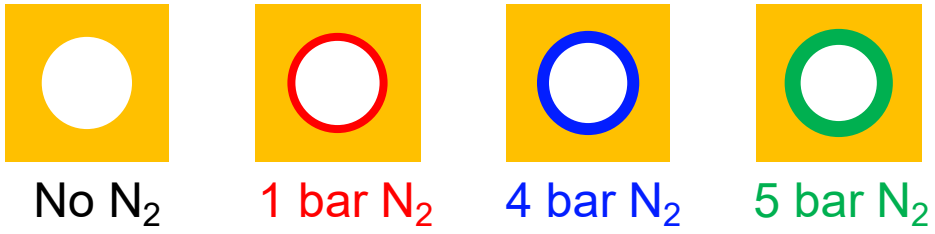
1.8 g of Zeolite Na/13X was placed in 2 mm flow-through TiZr cell (sample kept in Ar glovebox after drying at 160°C for 48 hrs)

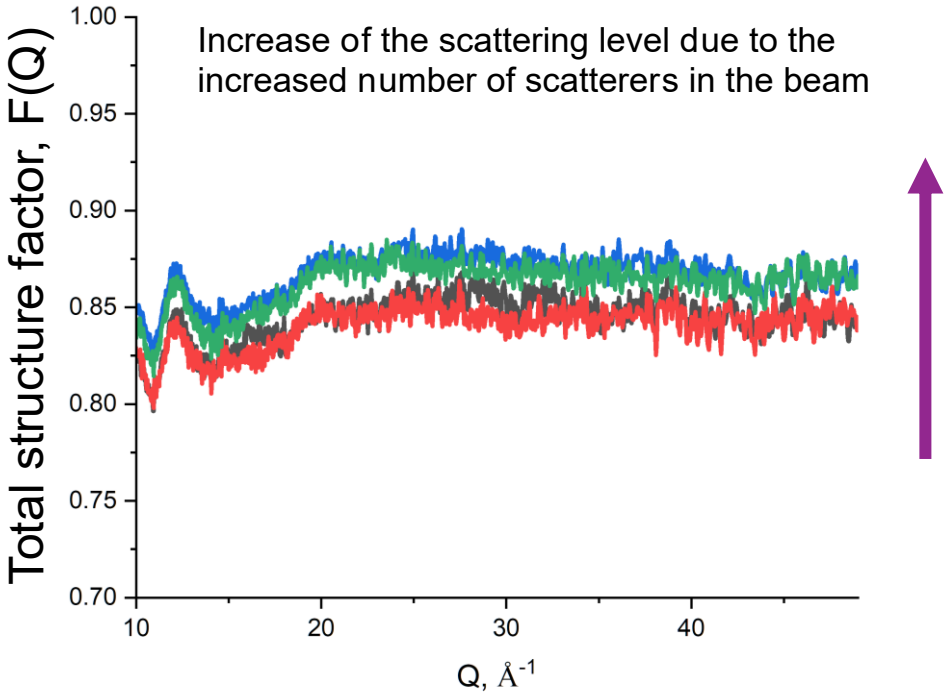
- ✓ Evacuation of zeolite
- ✓ Depositing gases at different pressures (up to 5 bar)
- ✓ Flushing the sample with Ar
- ✓ Monitoring a break-through curve *via* Mass Spectrometer



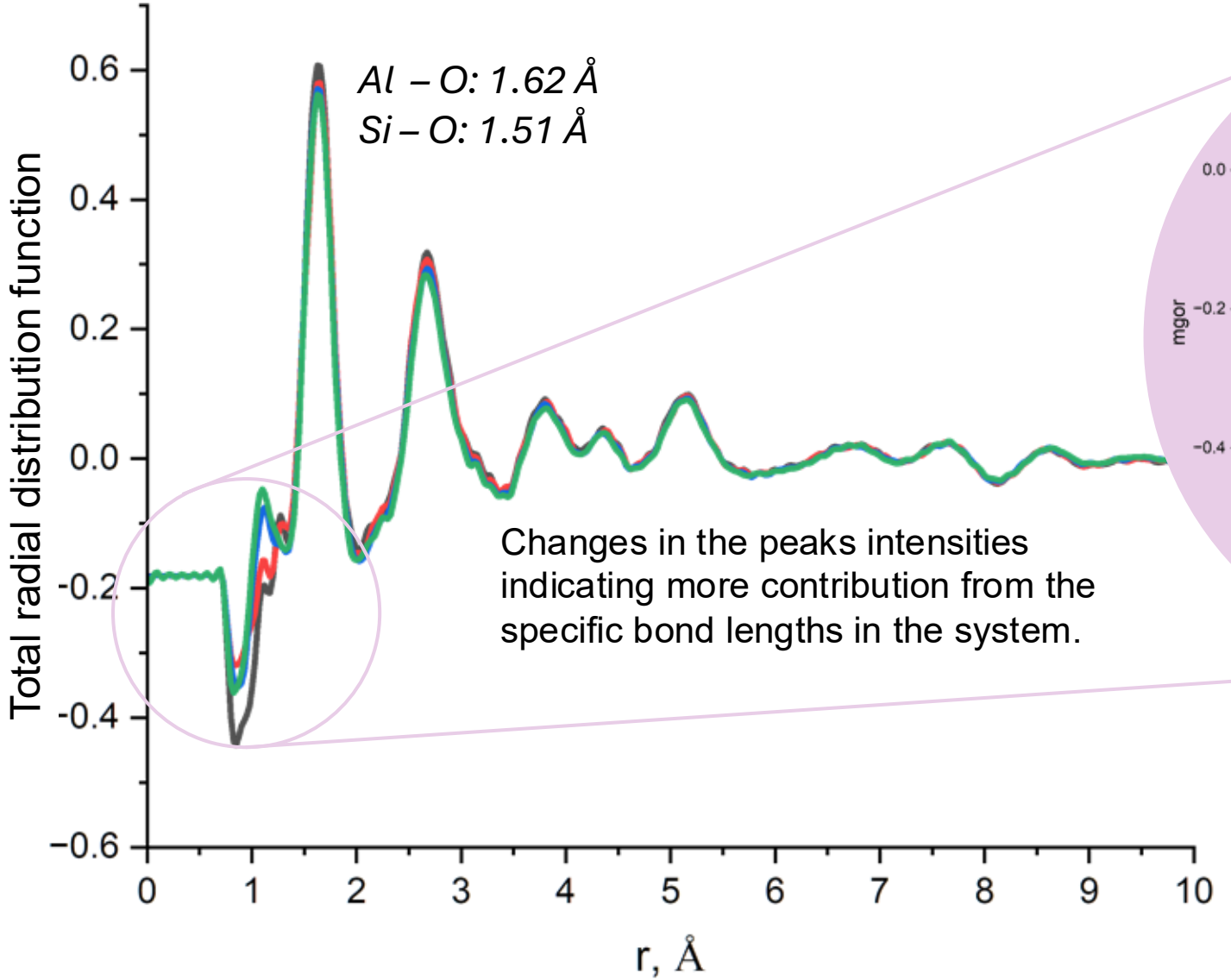
Structural patterns F(Q): 13X vs. 13X +N_2





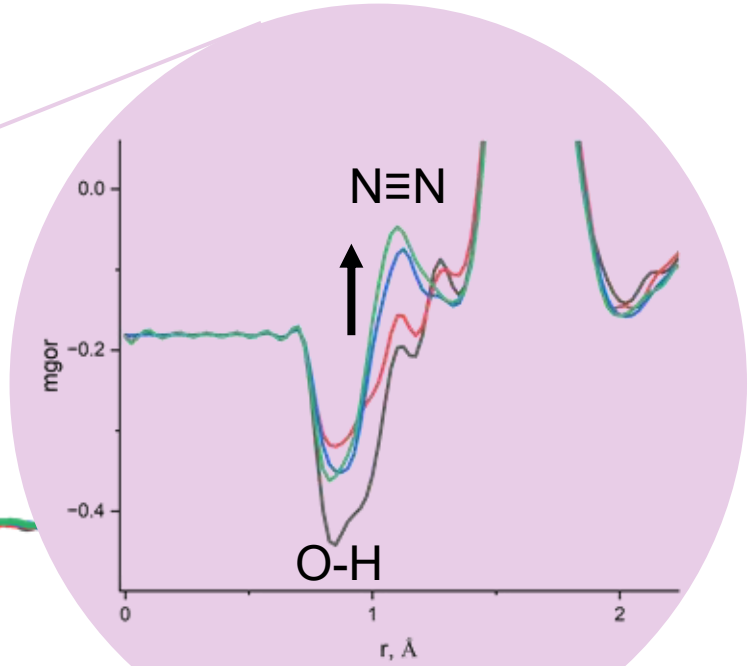


Radial distribution functions, g(r)

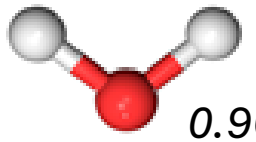


Al – O: 1.62 Å
Si – O: 1.51 Å

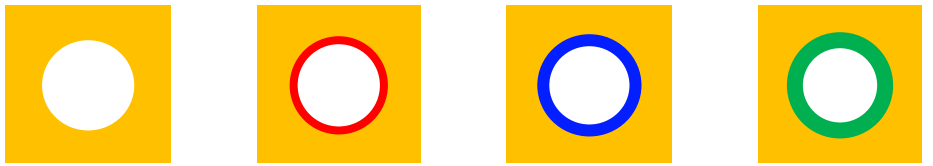
Changes in the peaks intensities indicating more contribution from the specific bond lengths in the system.



1.10 Å

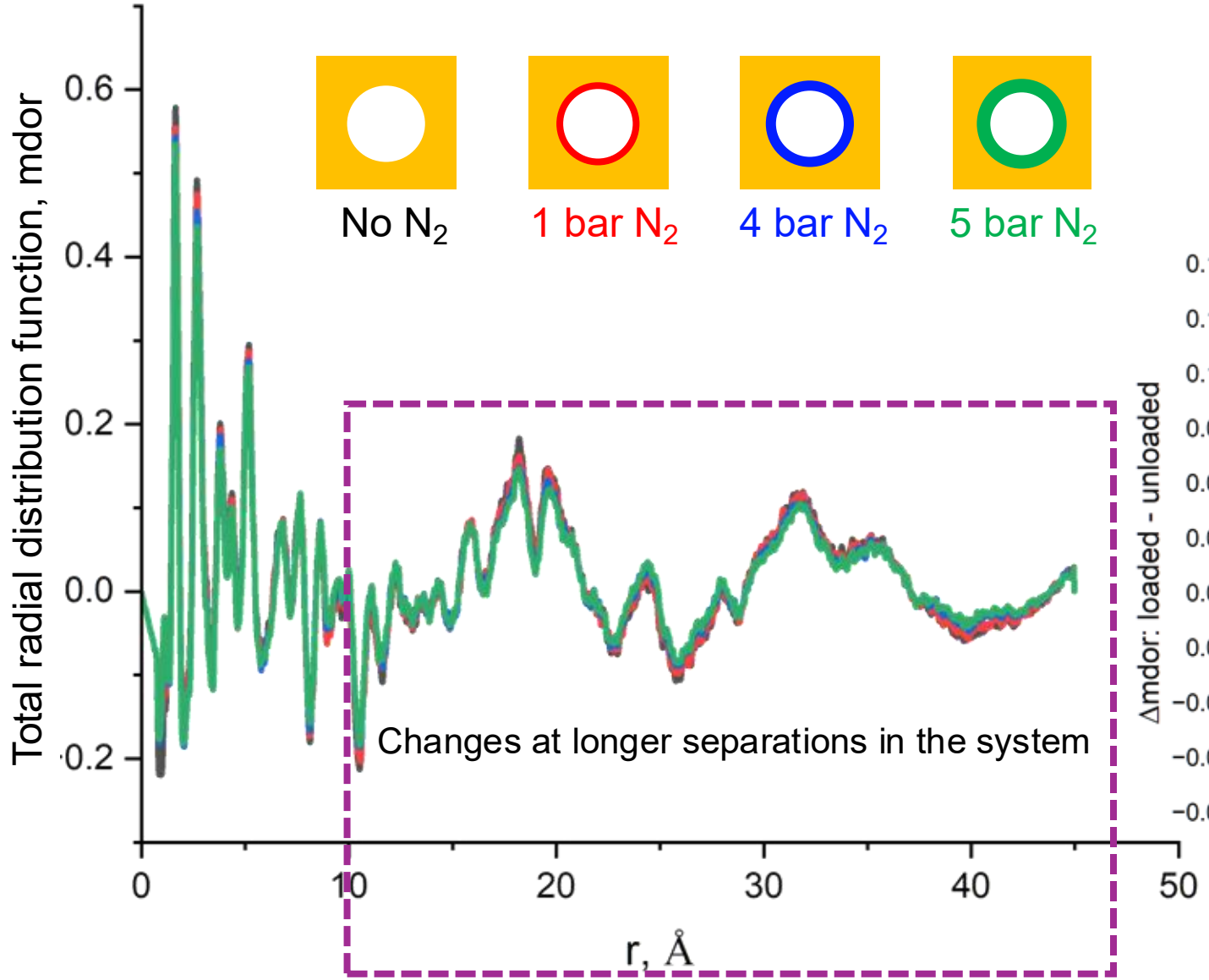


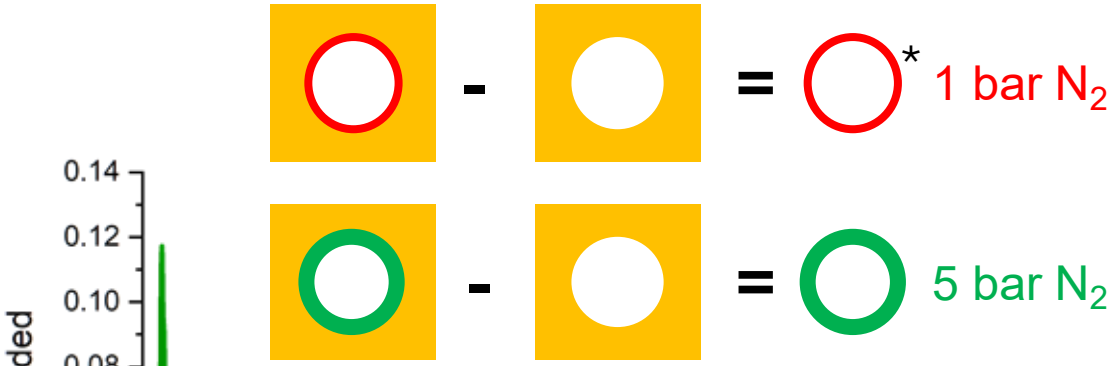
0.96 Å



No N_2 | 1 bar N_2 | 4 bar N_2 | 5 bar N_2

Radial distribution functions – high r



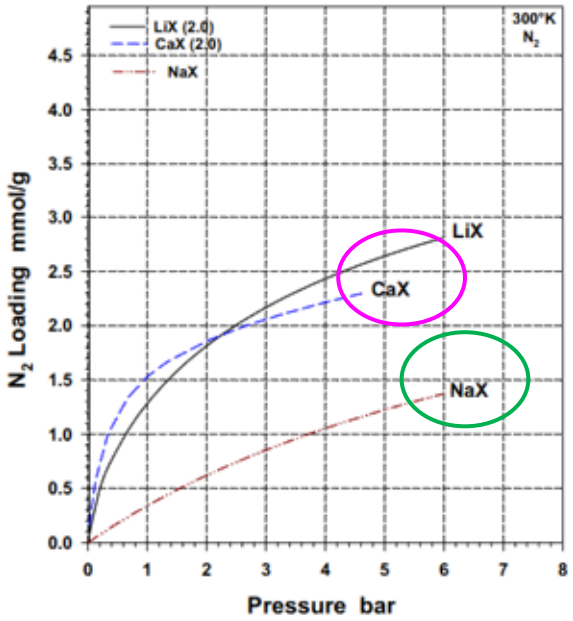


* Contribution from gas-gas and gas-surface interactions

Adsorption of N_2 in 13X: Na^+ *vs.* Ca^{2+}

Atomic radius:

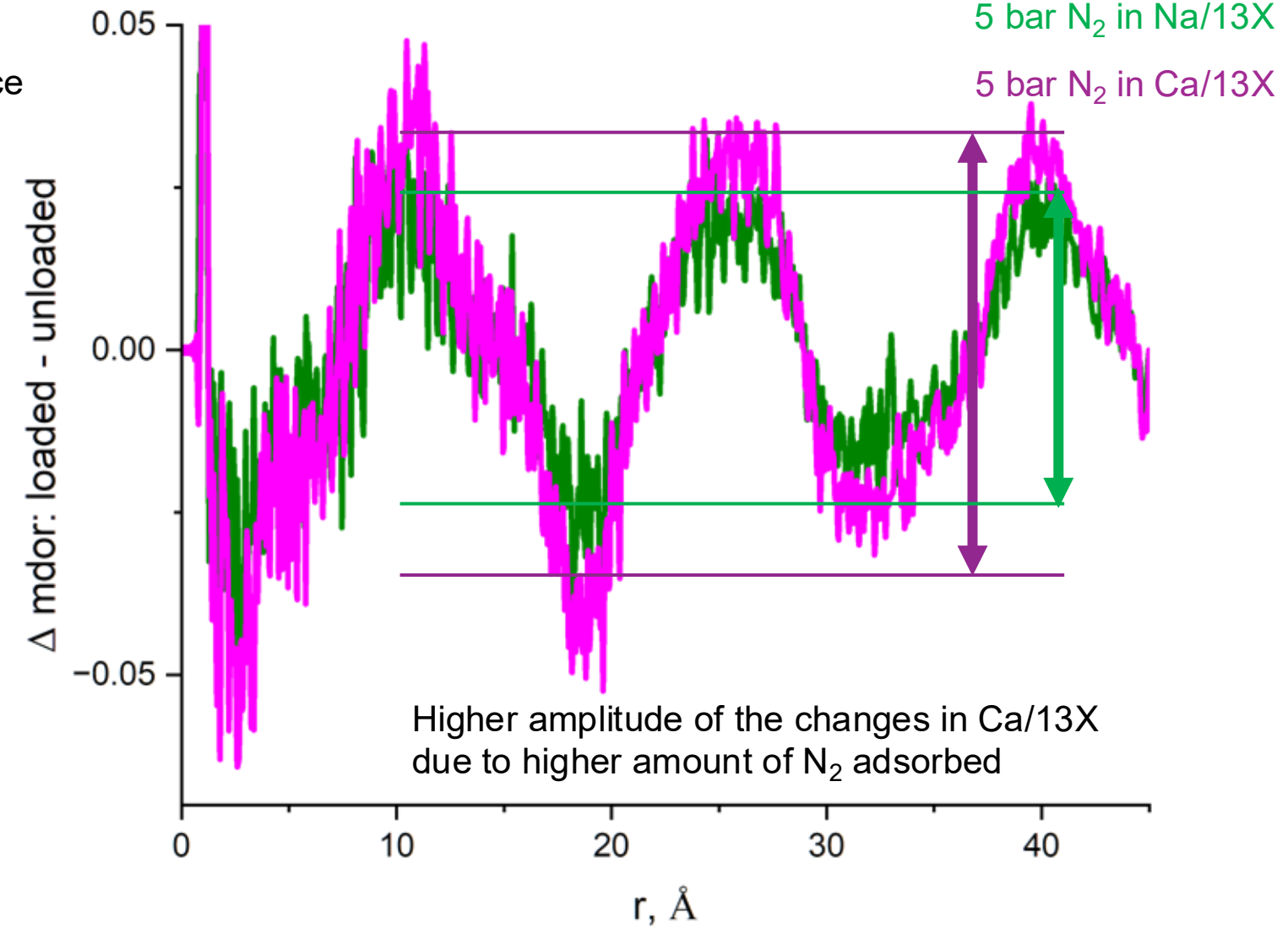
- Na+ 190 pm
- Ca^{2+} 194 pm but also higher valence
- Li^+ 167 pm



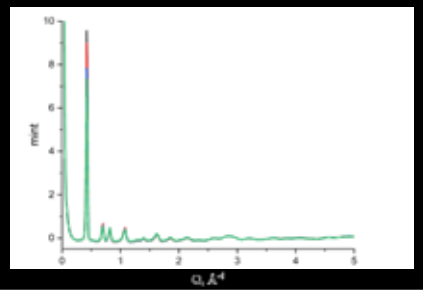
(Ackley, Adsorption 2019, 25, 1437)

XRF analysis on our samples:

- Zeolite **Na**/13X: 60 Na^+ : 3 Ca^{2+}
- Zeolite **Ca**/13X: 32 Ca^{2+} : 2 Na^+



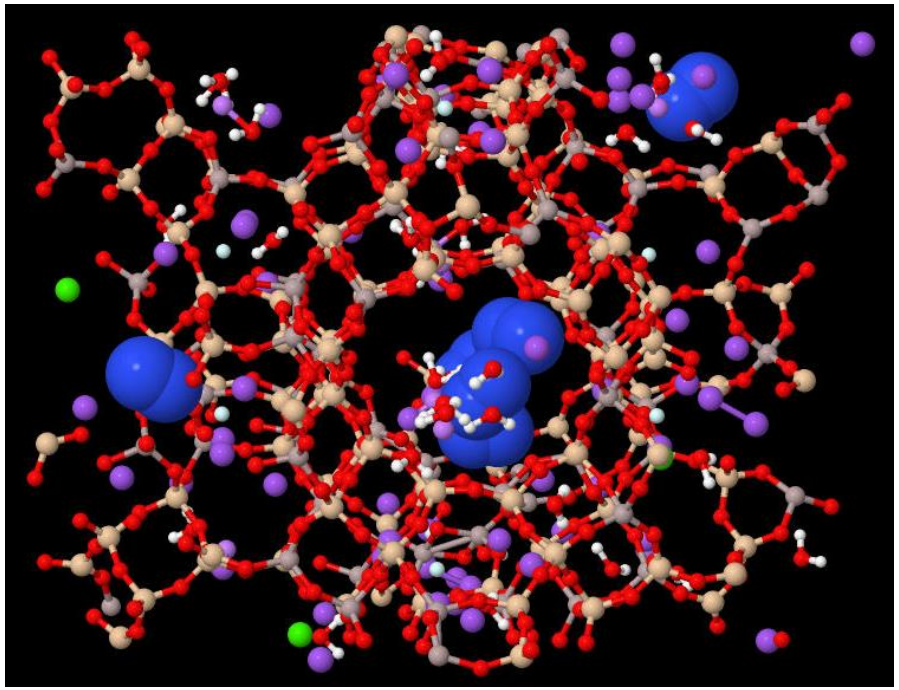
Experimental data



Chemical constraints:

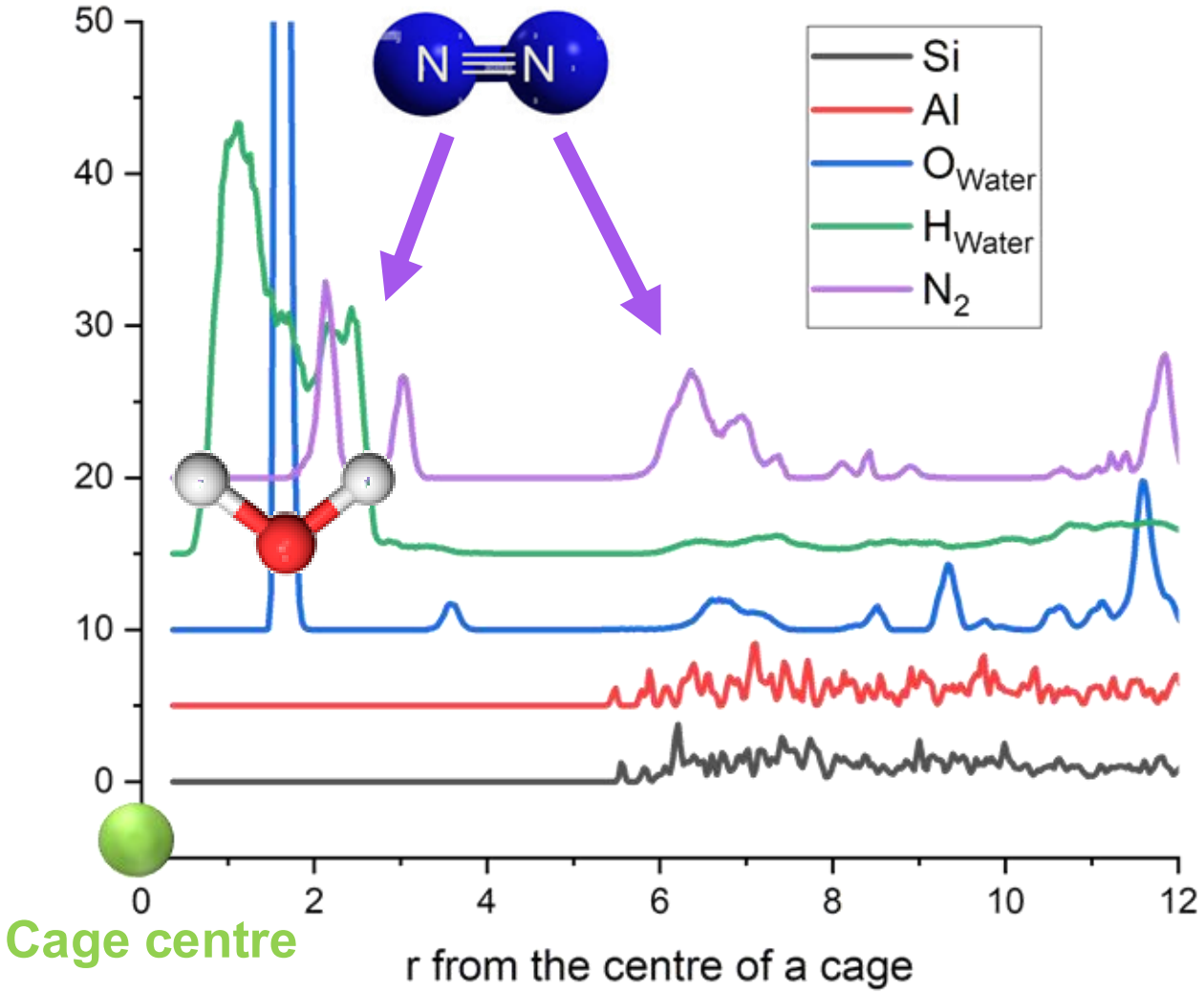
LJ potential, charges, density

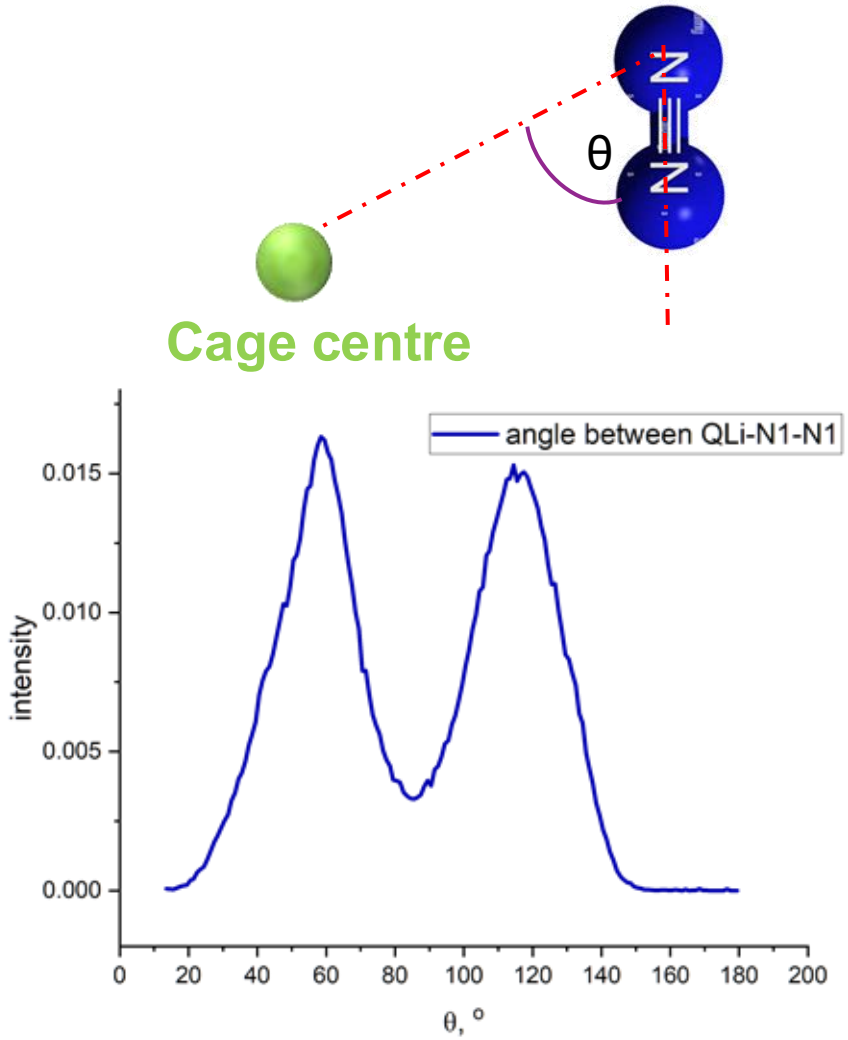
Empirical potential structure refinement



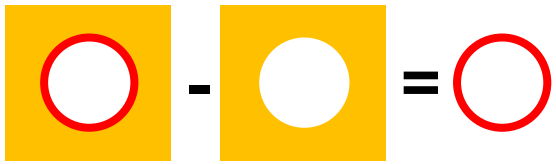
Average structure of the sample

Model driven by data – 5 bar N_2 in 13X



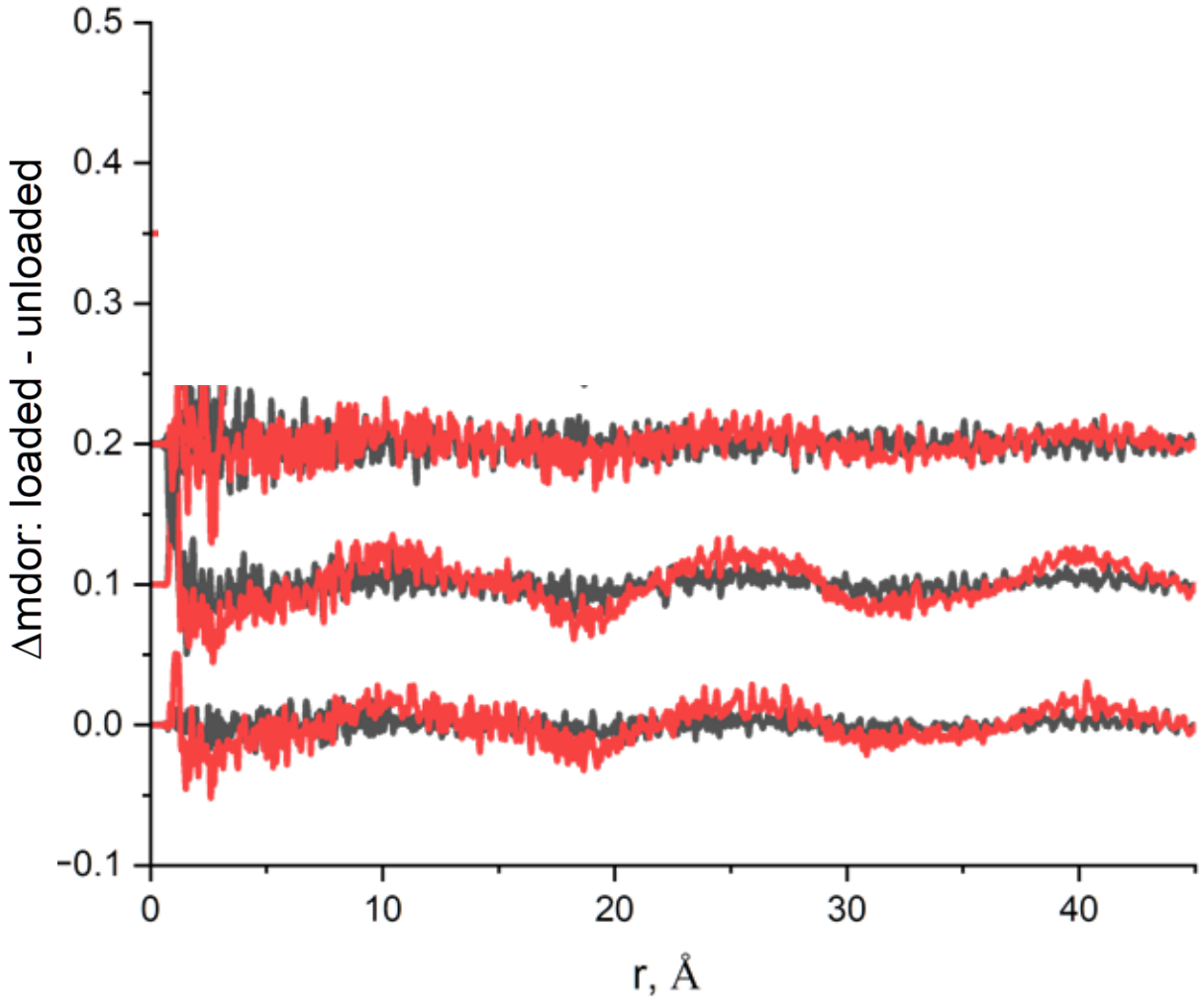


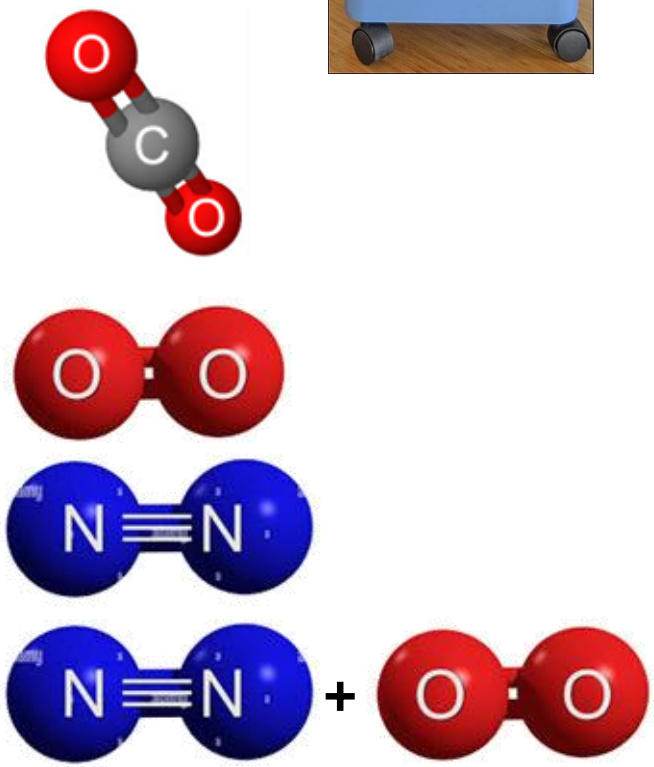
Adsorption of gases in Zeolite Na/13X



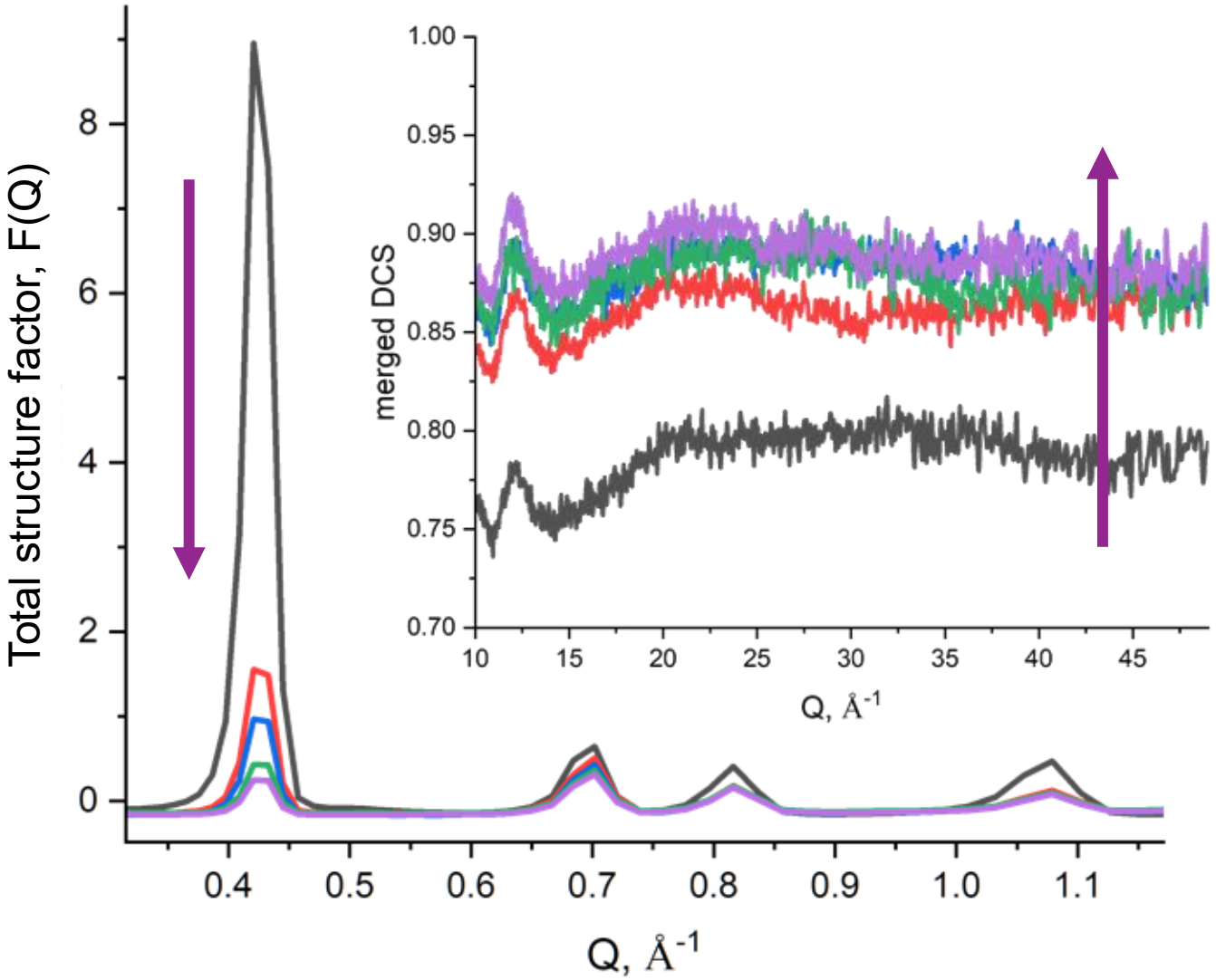
Data shown for **1 bar** and **5 bar** for each gas/gas mixture:

- O_2 at 1 and 5 bar – no significant changes
- N_2 at 1 bar – no significant changes
- N_2 at 5 bar – visible changes
- N_2/O_2 at 1 bar – no significant changes
- N_2/O_2 at 5 bar – visible changes similar to N_2 at 5 bar
- CO_2 at 1 and 5 bar – significant changes





Adsorption of CO_2 in Zeolite Na/13X



No CO_2

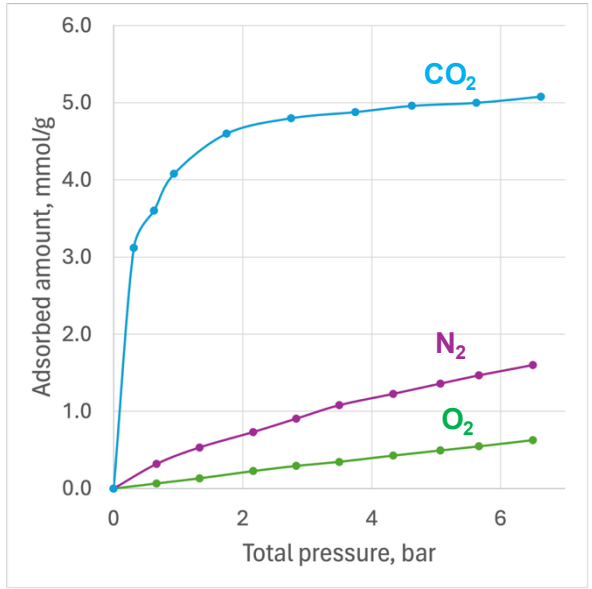
0.5 bar CO_2

1 bar CO_2

4 bar CO_2

5 bar CO_2

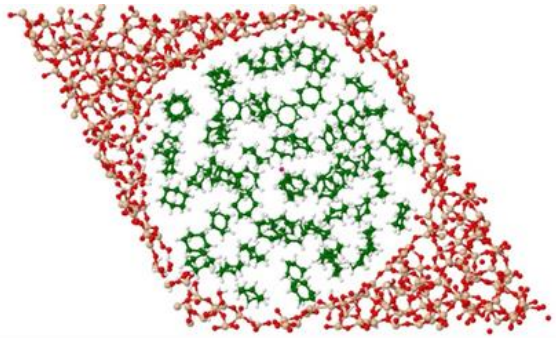
Very significant changes in Bragg peak intensities while the pressure of CO_2 increases, and in scattering level.



Conclusions

- *TNS conducted at NIMROD proves to be the experimental technique that can follow gas adsorption at the molecular scale:*
  - *Qualitatively & Quantitatively (models refined by data)*
- *Suggested by the literature trends were captured by TNS results:*
  - *Stronger CO_2 adsorption*
  - *Impact of a counter-ion in the framework*
  - *Preferential adsorption of N_2 over O_2*
- ***But the data analysis is difficult***

Empty framework



Framework with fluid

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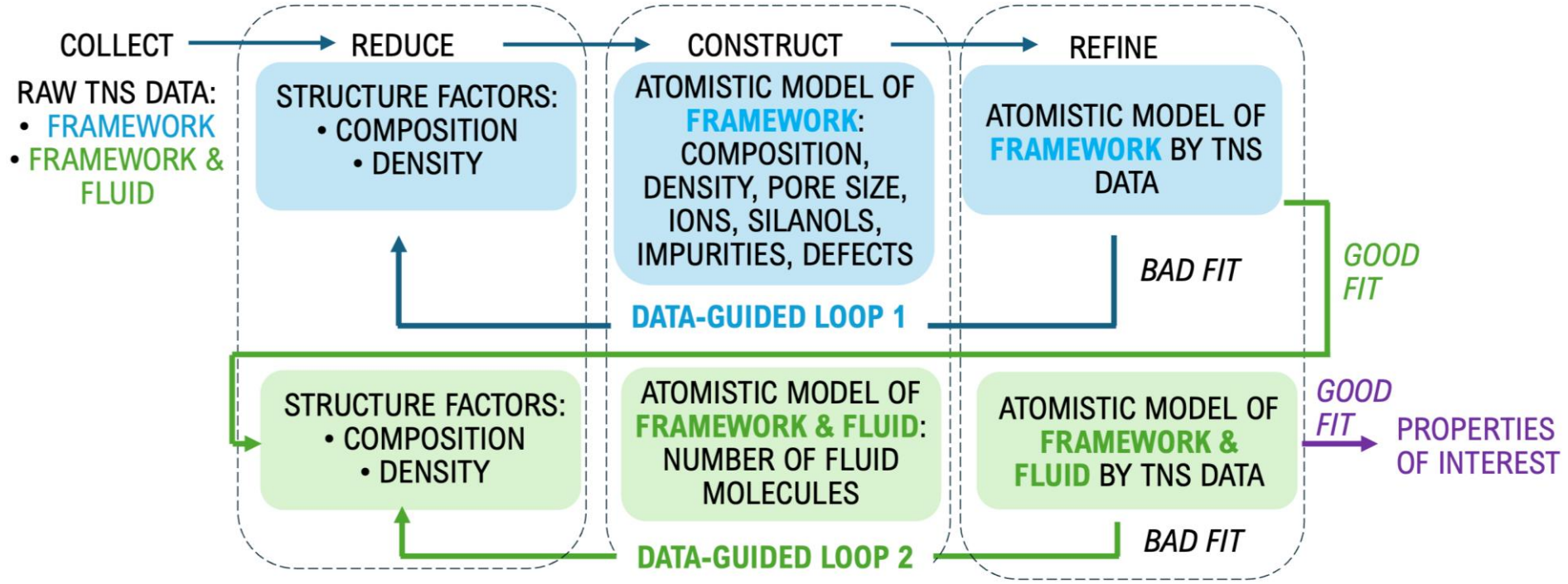
Data analysis



Heterogeneity of a sample, inaccessible pores, different pore filling

Dissolve

Tristan Youngs, Marta Falkowska
3.5 years ISIS-UoM PhD Studentship
on Revealing Solvents Under Confinement